

OC and EC analyzed in PM₁₀, PM_{2.5} and PM₁ using thermo graphic and thermo-optical method at Melpitz site in Germany – a two year comparison

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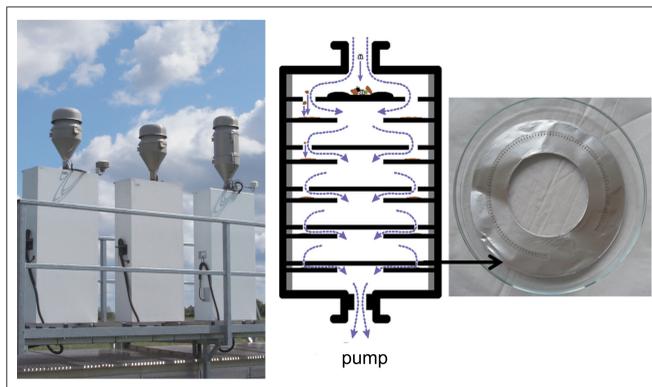


Figure 1: The HV-filter-samplers for PM₁₀, PM_{2.5} and PM₁ at Melpitz site for daily samples on quartz fibre filters and the five stage BERNER-impactor for sampling on Al-foils for several days. The Al-foil for stage 5 is shown (particles with 0.05 to 0.14 µm aerodynamic diameter).

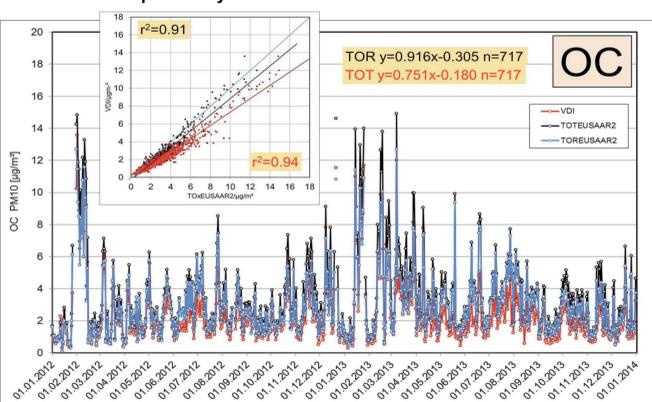


Figure 2: Example for the calculation of the empirical conversion equations for OC in PM₁₀ over the whole time (2012 and 2013).

		[OC; EC; TC] _{TGVDI} = m _x × [OC; EC; TC] _{TOTEUSAAR2} + n _x					
		x = Reflectance or Transmittance					
		m _R	n _R	r ²	m _T	n _T	r ²
all days	OC	0.925	-0.279	0.92	0.751	-0.179	0.95
	EC	0.500	0.378	0.66	1.088	0.343	0.58
	TC	0.840	0.008	0.98	0.840	0.008	0.98
SUMMER days	OC	0.666	0.125	0.84	0.605	0.098	0.87
	EC	0.728	0.305	0.55	1.570	0.307	0.44
	TC	0.786	0.123	0.93	0.786	0.123	0.93
WINTER days	OC	0.987	-0.257	0.97	0.776	-0.163	0.97
	EC	0.504	0.308	0.73	1.014	0.299	0.77
	TC	0.848	-0.021	0.99	0.848	-0.021	0.99

The conversion equations depends from season – in approximation conversion equations can be derived monthly.

Figure 3: Calculation of conversion factor m, intercept n and r for all days and selected for Winter: November until April and Summer: May until October over the whole time (2012 and 2013).

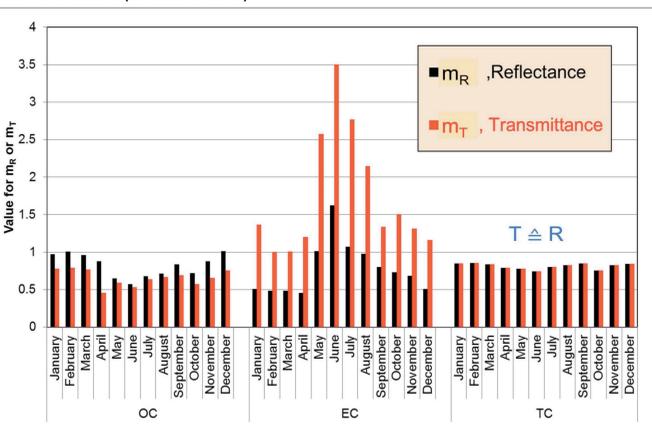


Figure 4: Calculation of monthly conversion factors for reflectance (m_R) and transmittance (m_T) for OC, EC and TC for all sizes over the two years with parallel carbon analysis for Melpitz site. (2012 and 2013).

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- 1) European Monitoring and Evaluation Programme
- 2) Aerosol, Clouds, and Trace gases Research InfraStructure Network

Method and Motivation

Since 2003 organic (OC) and elemental carbon (EC), in sum total carbon (TC), were quantified at quartz-fibre filters (HV) with an analyzer, C/S-Max, Seifert Instruments, Germany using a variation of the Guideline VDI2465 (Part 2). This thermographic method (TGVDI) can be used for quartz filters from high-volume-samplers and also for samples on aluminum foils (melting point=660° C) using in BERNER-impactors (IP), because the maximum temperature doesn't exceed 650° C (Figure 1). Charring processes cannot be accounted here (Spindler et al 2012). A thermo-optical method (TO) using the Lab OC-EC Aerosol Analyzer by Sunset Laboratory Inc. U.S.A. was introduced at TROPOS in 2012 together with temperature protocol EUSAAR2 (final temperature 850° C, Cavalli et al 2009). The correction value for „pyrolytic carbon“ is achieved from measurement of transmission (TOT) or reflectance (TOR)(Chow, et al. 2004, Bautista VII et al. 2015) of the sample using a laser (wavelength 678 nm). In European networks, e.g. EMEP¹) and ACTRIS²), TOTEUSAAR2 is the preferred technique for quartz fibre filters. We derive conversion equations from two years parallel analysis of daily samples following TGVDI and TOTEUSAAR2 or TOTEUSAAR2 to convert long-time measurements of HV samples of Melpitz site from yesteryears (TG to TO). Furthermore mean mass absorption cross sections were calculated from measured particle light absorption coefficients and EC quantification by the different TG and TO methods.

Experimental and Results

The Melpitz site operated by TROPOS is located in the lowlands of Eastern Germany (12°56'E, 51°32'N, 86 m a.s.l.). The place represents the regional background in Central Europe (Spindler et al. 2012 and 2013).

The daily HV samples on quartz fibre filters (every day for PM₁₀ and PM_{2.5} and every six days for PM₁) were taken at Melpitz site using three HV samplers DIGITEL DHA-80 (Walter Riemer Messtechnik, Germany).

From the two year data set 10 days with more than 5 µm³ EC (TGVDI) in PM₁₀ were eliminated because the transmission for TOTEUSAAR2 is here very low. The calculation of conversions equations was done following as y=mx+n, equation 1 (compare the example for OC in Figure 2):

$$[OC; EC; TC]_{TGVDI} = m \times [OC; EC; TC]_{TOTEUSAAR2} + n \quad (1)$$

The conversion factor m and the intercept n were calculated for OC, EC and TC and for the size classes PM₁₀, PM_{2.5} and PM₁ for all days. The correlations r² for TOT (PM₁₀) are for OC, EC and TC 0.94, 0.58 and 0.98, respectively. Alternatively EC can be calculated as EC=TC-EC. The results for TOR and TOT show that the conversion equations depends not essential on particle size and can be calculated for all sizes in one step. The conversion variable m depends on the season (Winter: November until April, Summer: May until October), compare Figure 3. As a compromise the conversion equations for OC, EC and TC were derived for the twelve month in a year using the 2012 and 2013 monthly data for all sizes. The conversion factors for EC (TOTEUSAAR2) show a strong variation over the year for the rural site Melpitz. The high values in summer are caused by a relative high amount of „pyrolytic carbon“ (PC) that is formed by charring of OC (TGVDI) (Figure 4). Figure 5 and 6 shows the variability of the EC/OC ratio over the year for the TGVDI and TOTEUSAAR2 and TGVDI and TOTEUSAAR2, respectively. The lower EC/OC-ratios where found in the summer. The spreading for the TGVDI is much higher as for the thermo-optical method and the detection of PC by reflectance provides a much higher EC/OC ratio as for transmission, especially in winter it reaches the values for TGVDI. For an independent estimation which off-line method gives more realistic OC concentrations the OC measurement of PM₁ filter-samples where compared with online AMS measurements (Figure 7). Because AMS provides OM the ratio OM/OC was calculated based on the elemental analysis of the high resolution mass spectra (Canagaratna et al. 2015). For samples from different regions and seasons it can be found that the thermo-optical method with transmission (TOTEUSAAR2) gives the most realistic OC concentrations in comparison to TGVDI or TOTEUSAAR2. This method provides the highest OC concentrations and a lower EC/OC ratio compared to TOTEUSAAR2 and TGVDI (Figure 5 and 6).

Figure 8 shows an example for the estimation of quasi TOTEUSAAR2 values for OC and EC from long-term HV-filter measurements of OC and EC using TGVDI. The recalculation was done using monthly conversion equations derived from 2012 and 2013. So historical data for OC and EC measurements by TGVDI can be compared with the new introduced method and continued in future for Melpitz site as TOTEUSAAR2 OC-EC-measurements.

The particle light absorption coefficient in PM₁₀ σ_{ap} measured with a Multiangle Absorption Photometer (MAAP 637 nm) shows an annual variation in the range 0.2 and about 30 Mm⁻¹. It is common to calculate Black Carbon (BC) from σ_{ap} using a constant mass absorption cross section of 6.6 m²g⁻¹. A comparison between σ_{ap} and results of the used different EC measurements here for 2012 and 2013 allows to calculate mass absorption cross sections for the different month (equation 2, Figure 9). The mass absorption cross section (α_C) mostly depends on

$$\sigma_{ap} = \alpha_{C[TGVDI, TOTEUSAAR2]} \times [BC], [EC]_{[TGVDI, TOTEUSAAR2]} ; x \triangleq T \text{ or } R \quad (2)$$

EC measurement method, but also on season. The monthly derived α_C shows lower values for summer as for winter. The annual variation is mostly distinct for TGVDI.

Summary

- We can derive mean conversion equations for OC, EC and TC. They do not depend on particle size (range PM₁₀ to PM₁) but from season.
- As a compromise conversion equations were derived monthly.
- The thermo-optical method can give a more stable split for OC and EC. A comparison with AMS measurements for OC in PM₁ give hints for more realistic OC quantifications using transmittance.
- EUROPE has unified the OC-EC-Determination for the future to the TOTEUSAAR2 method in March 2015.

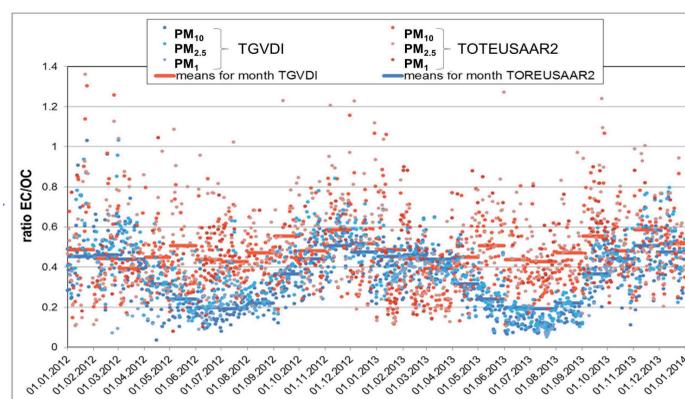


Figure 5: Daily ratios of EC/OC in 2012 and 2013 for PM₁₀, PM_{2.5} and PM₁. Method TGVDI in comparison to TOTEUSAAR2.

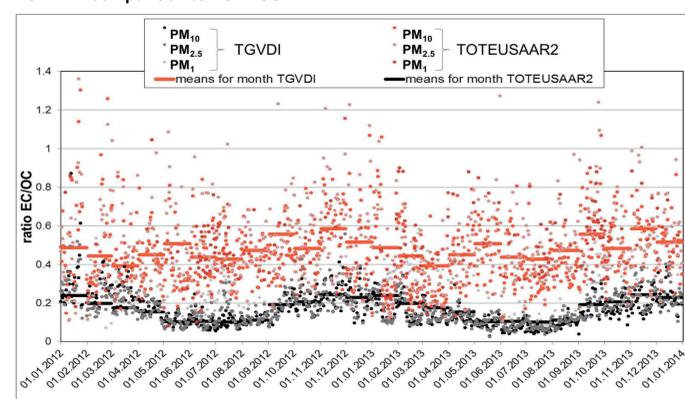


Figure 6: Daily ratios of EC/OC in 2012 and 2013 for PM₁₀, PM_{2.5} and PM₁. Method TGVDI in comparison to TOTEUSAAR2.

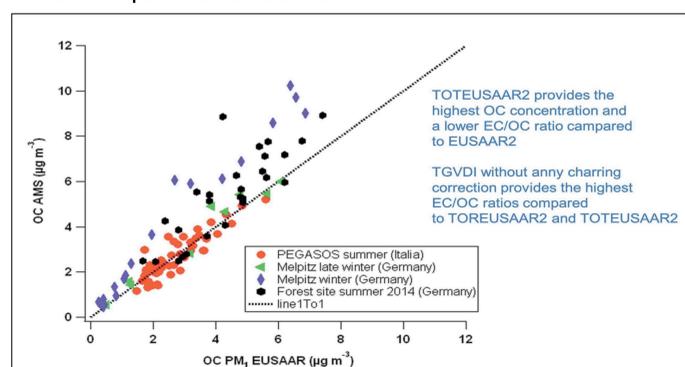


Figure 7: OC PM₁ off-line samples analyzed with TOTEUSAAR2 vs. AMS on-line measurements.

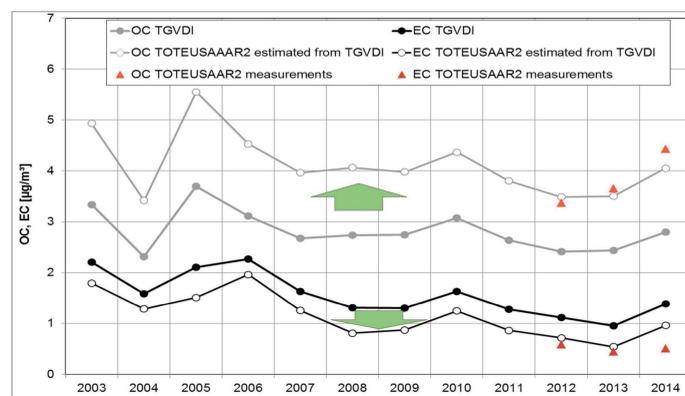


Figure 8: Long-term HV-filter measurements for OC and TC for Melpitz site using TGVDI (open circles) and estimation as results from TOTEUSAAR2 (full circles). The recalculation was done using monthly conversion equations derived from 2012 and 2013 (EC was calculated via TC-OC). For 2012-2014 the yearly means for direct TOTEUSAAR2 measurements are shown (triangles). All data are yearly means.

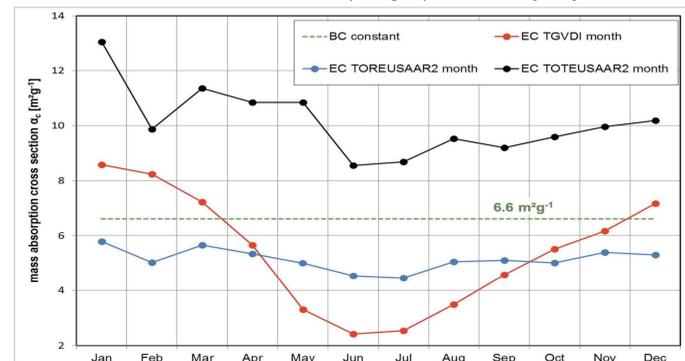


Figure 9: Monthly Mass Absorption Cross Section (σ_{ap}) derived from the particle light absorption coefficient measured with a MAAP for PM₁₀ using the EC quantification by TGVDI, TOTEUSAAR2 and TOTEUSAAR2. The common used constant σ_{ap} of 6.6 m²g⁻¹ is shown.

